Indian J. Phys. **66A** (5), 645-651 (1992)

Structural studies on some basic ligands : precursors for synthesising binuclear metal complexes

Tanusree Kar and S P Sen Gupta
Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Calcutta – 700 032, India

Received 16 September 1991, accepted 25 September 1991

Abstract : Results of the structural and molecular studies of three basic ligands namely, (I) 2-hydroxy–5–methyl–isophthalaldehyde $C_9H_8O_3$, (II) 2–acetyl–6–benzoyal–4–methyl phenol $C_{16}H_{14}O_3$ and (III) 2,6–dibutyryl–4–methyl phenol $C_{15}H_{20}O_3$, which are precursors for synthesising macrocyclic ligands, are reported here alongwith a discussion on other related compounds which exist in the literature. All the three compounds are characterized by a strong intra-molecular hydrogen bonding, which becomes stronger with the elongation of side chains. It is further apparent that, with the additions of bulky groups or side chains, the compounds transform to lower symmetry (i.e. orthorhombic ⟶ monoclinic ⟶ triclinic) as far as the crystalline lattice structure is concerned.

Keywords : Organic compounds, conformations, intra-molecular hydrogen bonding.

PACS Nos. : 61-10.–i, 61.10.My

1. Introduction : Chemical Aspects

It has become interesting to study the bi-nuclear metal complexes derived from the condensation products of 4-methyl–2,6–diformyl phenol [1] with various bi- and poly functionized molecules [1–3]. These studies were made to address basically to have (i) correlation of magnetic interactions with structural parameters, (ii) selective fixation and transport of substrates, (iii) catalysis of multicenter-multielectronic processes, and (iv) condensation of different substrates brought together and held in proximity. More recently, there is growing awareness, to design suitable binuclear copper(II) complexes that would mimic the behaviour of emigmatic type 3 copper proteins particularly homocyamin [4–9].

It may be mentioned that all the reported studies are concerned with the metal complexes derived from the condensation products of 4-methyl-2,6-diformyl phenol, but nothing is known about other homologues namely, 4-methyl-2,6-diacyl/benzoyl phenol. In our Inorganic Chemistry division of this Institute, Mondal and Nag [10–12] have undertaken an extensive programme of investigating binuclear complexes of later homologues. In the scheme (Figure 1) synthetic strategies that have been adopted by these workers to generate binuclear copper(II) complexes have been outlined. Compounds of the

type (4) contain two strongly antiferromagnetically coupled copper(II) ions and they undergo single step two-electron transfers [10], the features typical of EPR-silent copper(II) proteins. Contrary to these, complexes of the type 5, in which also copper(II) ions are very strongly coupled, however, undergo sequential electron transfers at two different potentials [11].

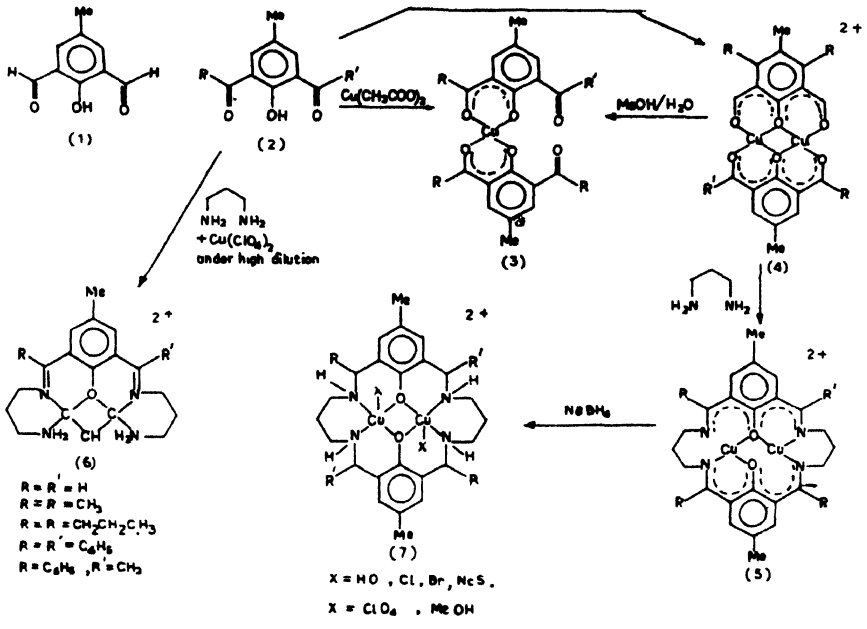

Figure 1. Synthetic strategies to generate binuclear copper complex

Complexes of the type (7) contain highly flexible ligand environment and therefore, would be expected to have interesting structural features. Structural analysis of the complexes (4) would be also highly desirable in as much as the two copper atoms are not in identical environment. Redox behaviour of the other type of complexes have turned out to be interesting and it has been shown from electrochemical vis-a-vis magnetic studies that in the coupled systems the triplet not the singlet state undergoes reduction [11]. In order to understand major as well as subtle difference in reactivity of these complexes, structural information about these species are very much essential.

In the light of all the above consideration, a series of structural investigations with these compounds have been undertaken by the present authors in the X-ray laboratory in collaboration with the chemistry division. This presentation summarizes the structural and molecular studies of the following three basic ligands namely,

(I) 2-hydroxy–5–methyl- isophthalaldehyde–$C_9H_8O_3$ (Figure 2), [13]

(II) 2-acetyl–6-benzoyl–4- methyl phenol–$C_{16}H_{14}O_3$ (Figure 3), [14]

(III) 2,6-dibutyryl-4–methyl phenol-$C_{15}H_{20}O_3$ (Figure 4), [15]

The second and third compounds are the extensions of the first one in which the two

hydrogen atoms in 1,3 positions are replaced by the different chemically active groups. The compounds are also important in synthesising macrocyles which would accommodate metal

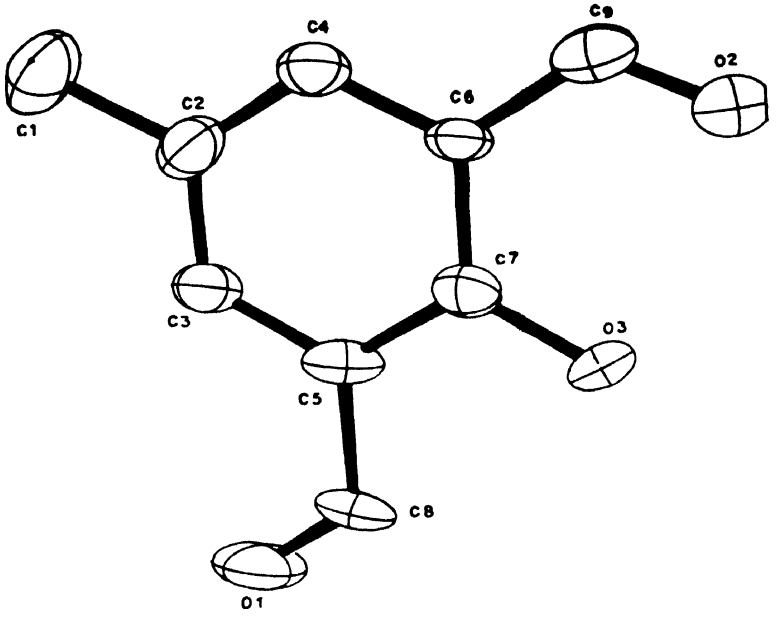

Figure 2. Ortep plot of 2 hydroxy–5–methyl isophthalaldihyde, $C_9H_8O_3$.

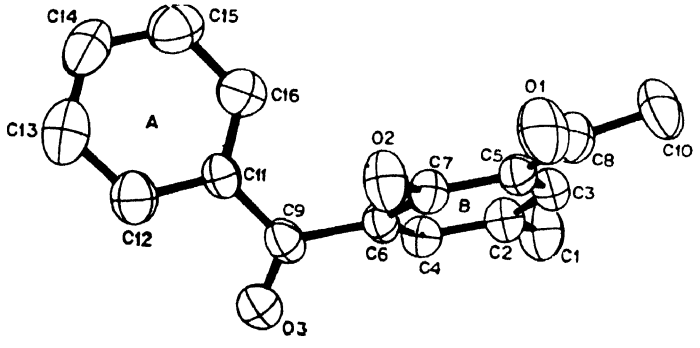

Figure 3 Ortep plot of 2-acetyl–6-benzoyal 4 methyl phenol, $C_{16}H_{14}O_3$.

atoms and serve as useful biological models. Cell constants and other crystal parameters for the compounds are summarized in Table 1. The intensity data (L–P corrected) for all the three compounds were collected on a CAD-4 Enraf-Nonius diffractometer at the RSIC (Bose Institute, Calcutta). All the structures have been solved by Direct methods using the programmes MULTAN-78 [16] and MULTAN-80 [17]. The relevant bond lengths (standard deviations in the range of 0.005 – 0.01 Å) and planarity of the molecules for all the three compounds are summarized in Table 2.

Table 1. Crystal data.

Parameters	Compound I	Compound II	Compound III
Molecular formula	$C_9H_8O_3$	$C_{16}H_{14}O_3$	$C_{15}H_{20}O_3$
λ (Å)	0.7114	0.7114	0.7114
a (Å)	25.998(8)	11.836(5)	8.12(1)
b (Å)	7.555(2)	8.706(2)	9.39(1)
c (Å)	3.944(2)	15.365(4)	10.31(0)
α°	90	90	103.5
β°	90	123.05(3)	91.9
γ°	90	90	114.1(1)
V (Å)^3	774.7(5)	1327.09	690.84
D cal g cm^{-3}	1.41	1.27	1.19
Z	4	4	2
Space group	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$
No of observed reflections			
$Fo > 2\sigma(Fo)$	526	1587	804
R-factor (%)	9.1	6.7	9.9

2. Results and discussions

All the three structures are characterized by a very strong intra-molecular hydrogen bonding between phenolic oxygen and the carbonyl oxygen in conformity with the NMR and IR

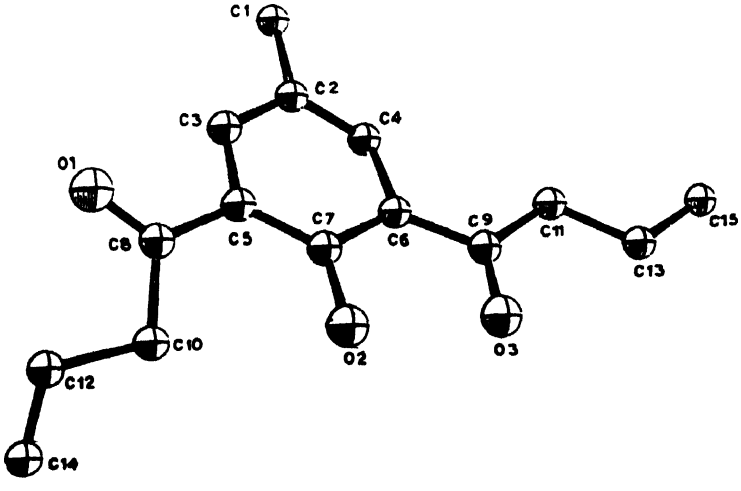

Figure 4. Ortep plot of 2,6-dibutyryl-4–methyl phenol, $C_{15}H_{20}O_3$.

spectra. This bonding is strongest for the compound III having lowest summetry ($P\bar{1}$). Though the chemically equivalent bond distances within the six membered rings are

identical, they have, however, undergone a slight deformation from the normal benzene ring geometry and this may be attributed to the effect of substituents. In compound II, though both the aromatic rings are equivalent in respect of bond lengths, the angular deviations in ring *B* are much more pronounced that those in ring *A*, and this may be due to the presence of more number of substituents in the molecules. The relation between the angular deviations and substituents effect was studied for compounds with mono- and di-substituted

Table 2. Relevant bond distance (Å) and planarity of benzene rings.

Parameters	Compound I	Compound II	Compound III
$C(Sp^2)$–$C(Sp^3)$ distance between methyl carbon and aromatic ring carbon	1.55	1.52	1.54
Average $C(Sp^2) - C(Sp^3)$ distance in the side chains	No $C(Sp^2) - C(Sp^3)$ bond in the side chain	1.47	1.49
Average $C(Sp^2)$–$C(Sp^2)$ distance between aromatic ring carbon and carbonyl carbon	1.46	1.48	1.46
Average C – C distance in the benzene ring	1.39	1.39	1.40
Average C = O distance	1.21	1.22	1.22
C–OH	1.36	1.36	1.35
Intra-molecular hydrogen bonding distance between phenolic oxygen and carbonyl oxygen	2.62	2.55	2.46
Planarity	Benzene ring is almost planar maximum deviation –0.02 Å	Both the benzene rings are planar and they are inclined with each other at an angle 108.8°	Benzene ring is planar, maximum deviation –0.01 Å

benzene rings [18, 19]. Another significant observation in all the three structures is the deviations of C—OH and C=O bond distances from their expected values, which can be explained by considering electron donation from hydroxyl group through the aromatic system to the carbonyl group which in turn strengthens the C—OH bond, weekens the C—O bond, and increases the negative charge on the carbonyl oxygen [20] resulting in an intra-molecular hydrogen-bonding causing a shortening in the C—OH bond and lengthening in C=O bond ffom their normal values. Similar observation can be had, for example, in the structure of 2,2'-dihydroxy benzophenone [20]. In all the above cases the C=O distance is legthened against the normal value (C=O) = 1.20 Å. The other $c(sp^2) - c(sp^3)$ distances in

the side chains show small positive and negative deviations from the normal expected value. The unusual short value (1.24 Å) for the distance between (C12 and C14) atoms towards the free end of one of the side chains in compound III, could only be attributed to the limited size of data and also to some disordering in the molecule, as evident from high thermal parameters (ORTEP PLOT, Figure 4) for the atoms concerned. The type of bond shortening with higher thermal parameters for atoms concerned have also been encountered in other structures [21, 22]. The planarity calculations show that the structure of compound I is almost planar. The planes of the two phenyl rings in compound II are inclined at an angle of 108.8°. This inclination is, however, expected since it tends to minimize the $\pi - \pi$ orbital overlap between the rings, and compares favourably with values observed in other diphenyl methane structure [23, 24]. In all the three structures, the molecules did not involve themselves with any inter-molecular hydrogen bonding, and all the structures are completely stabilized by the normal van der Waals forces.

3. Conclusions

(a) The molecular structure of all the three compounds (I, II, III) presented here have similar conformations as far as bond distances and angles are concerned.

(b) All the three structures are characterized by a strong intra-molecular hydrogen bonding and this bonding becomes stronger with the elongation of side chains (Compounds III). In the molecular packing there exists no inter-molecular contact involving hydrogen and the structures are stabilized by normal inter-atomic forces.

(c) With the additions of bulky groups or side chains, the structures transform to lower symmetry (i.e. orthorhombic ——→ monoclinic ——→ triclinic).

Acknowledgment

We thank Professor K Nag and his colleagues of the Inorganic Chemistry Division, Indian Association for the Cultivation of Science for providing single crystals of the compounds and many helpful discussions.

References

[1] U Casellato, P Vigato and M Vidali 1977 *Co-ord. Chem Rev* 23 31
[2] S E Groh 1976 *Inorg. Chem.* 15 227
[3] U Casellato, P Vigato, D E Fenton and M Vidali 1979 *Chem Soc Rev.* 8 199
[4] R R Gagne, C A Koral, T J Smith and M C Cimolino 1979a *J Chem. Soc* 101 4571
[5] R R Gagne, R P Kreh and J A Dodge 1979b *J Chem Soc* 101 6917
[6] R R Gagne, L M Hemling and J Kistenmacher 1980 *Inorg. Chem.* 19 1226
[7] R R Gagne, C L Spiro, T J Smith, W R Thies and A K Shiemke 1981 *J. Am. Chem. Soc.* 103 4073
[8] J Graybowski, P H Merrell and F L Vrback 1978 *Inorg Chem.* 17 3078
[9] J Grazybowski and F L Urbach 1980 *Inorg. Chem* 19 2604
[10] S K Mondal and K Nag 1983a *Inorg Chem* 22 2567
[11] S K Mondal and K Nag 1983b *J. Chem. Soc Dulton Trans.* 2439
[12] S K Mondal and K Nag 1984 *J. Chem. Soc. Dulton Trans.* 2839
[13] Tranusree Ray and S P Sen Gupta 1982 *Cryst. Struct. Commun* 11 59

[14] Tanusree Ray and S P Sen Gupta 1981 *Cryst. Struct. Commun.* **10** 1123

[15] Tanusree Ray and S P Sen Gupta 1986 *Indian J. Phys.* **60A** 110

[16] P Main, S E Hull, L Lessinger, G Germain, J P Declercq and M M Woolfson 1978 *MULTAN 78. A system of computer programmes for the Automatic Solution of Crystal Structures from X-ray Diffraction Data* (Universities of York and Louvain, England)

[17] P Main, S J Fiske, S E Hull, L Lessinger, G Germain, J P Declercq and M M Woolfson 1980 *MULTAN 80. A system of computer programmes for the Automatic Solution of Crystal Structure from X-ray Diffraction Data* (Universities of York and Louvain, England)

[18] A Domenicano, A Viciago and C A Coulson 1975 *Acta Cryst* **B31** 221

[19] A Domenicano, P Mazzeo and A Vaciago 1976 *Tetrahedral Lett* **13** 1029

[20] E O Schlemper 1982 *Acta. Cryst.* **B38** 1619

[21] M R Smith, R A Zingaro and E A Meyers 1971 *J Organometal Chem* **27** 341

[22] Y Le Page, E J Gabe, L R C Bercley and J M Dust 1981 *Acta Cryst.* **B37** 976

[23] B Chaudhuri and A Hargreaves 1956 *Acta Cryst* **9** 793

[24] E J W Whittaker 1953 *Acta Cryst* **6** 714